Indian J. Phys. 43, 674–679 (1969)

On the variational states and the ground state energy

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(*Received* 8 *October* 1969)

The object of this paper is to show that the estimate of the ground state energy may be considerably improved with the help of another variational state, in addition to that used for the estimation of the ground state energy.

Introduction

In many applications of quantum mechanics to problems in physics and physical chemistry, use is made of variational states to determine approximately the ground state energy, as well as those of the neighbouring excited states ; the corresponding expectation values, which are extremized, are taken as approximate eigen-values. A little critical examination reveals that if two or more variational states and the corresponding estimates of the eigen-values are known, in general, it is possible to obtain a much better estimate of the ground state energy. This is possible only because of the absolute minimum character of the ground state energy, which is the lowest eigen-value. The object of this paper is to show explicitly, how this can be done with the knowledge of two variational states and respective expectation values of the energy. This is accomplished by finding new variational states from the two known variational states which minimizes the expectation value of energy. As it is expected, in general, this further lowers the expectation value. The method can be easily extended to the case where more than two variational states are known.

In the following section the new variational states with a real parameter and the improved estimates of the expectation values are worked out. The next section is devoted to the algebraic significance of the method. It contains further discussions on the practical use and the possible generalization of the method. The paper is supplemented by an appendix in which the parameter introduced for the formation of the new variational state is no longer real. This does not change the basic nature of the result which is obtained with a real parameter, but further improves the estimate.

In short, it is shown here that in addition to the determination of the mutually orthogonal variational states for obtaining the ground state energy, a further restriction should be imposed that the Hamiltonian must be diagonalized in this subspace of the variational states. Since one of the diagonal element is less than the previous determination of the ground state energy, it is a better estimate of the latter, because of the absolute minimum property of the ground state energy.

THE VARIATIONAL STATES AND THE ESTIMATE OF THE EIGEN-VALUES.

Let H be the total Hamiltonian of the system and let ϕ_1 be the solution of the variation problem

$$\text{with} \quad \left.\begin{aligned} \delta(\tilde{\phi}.H\phi)&=0 \\ (\tilde{\phi}.\phi) &= 1, \end{aligned}\right\} \qquad ...(1)$$

$$\text{and let} \quad (\tilde{\phi}_1.H\phi_1)=E_1 \qquad ...(2)$$

So that E_1 may be taken as an estimate of the ground state energy. Further, let ϕ_2 be another solution of equation (1) such that

$$(\tilde{\phi}_2.\phi_1)=0 \qquad ...(3)$$

$$\text{and let} \quad (\tilde{\phi}_2 H\phi_2)=E_2 \qquad ...(4)$$

Thus E_2 which is greater than E_1 may be taken as an estimate of the energy of some neighbouring state (not necessarily the adjacent one).

Let us consider the new variational state

$$\psi=(\phi_1+\epsilon\phi_2)\,(1+\epsilon^2)^{-\frac{1}{2}} \qquad ...(5)$$

which is a linear combination of ϕ_1 and ϕ_2; it is normalized to unity. In order to avoid unnecessary complications we take ϵ to be a real parameter. In the appendix it is shown that the estimate of energy is further improved by taking ϵ complex. Now

$$(\tilde{\psi}.\,H\psi) = (E_1 + 2\epsilon k + \epsilon^2 E_2)\,(1+\epsilon^2)^{-1} \qquad ...(6)$$

$$\text{where} \quad 2\,k = (\tilde{\phi}_1.H\phi_2) + (\tilde{\phi}_2.H\phi_1). \qquad ...(7)$$

Since H is hermitian k is real, in general k is different from zero. In that case the expression (6), *qua* a function of ϵ, say $f(\epsilon)$, can be extremized. Since

$$\frac{df(\epsilon)}{d\epsilon}=\frac{2}{(1+\epsilon^2)^2}\left\{k\,(1-\epsilon^2)+\epsilon(E_2-E_1)\right\} \qquad ...(8)$$

the two extrema are given by

$$\epsilon_{\pm} = (E_2 - E_1 \pm \overline{E})/2k \qquad ...(9)$$

where

$$\bar{E} = | \{(E_2 - E_1)^2 + 4k^2\}^{\frac{1}{2}} | \qquad \ldots(10)$$

$$\frac{d^2 f(\epsilon)}{d\epsilon^2} = \mp 2\bar{E}(1 + \epsilon_{\pm}^2)^{-2} \qquad \ldots(11)$$

Hence, at ϵ_+ it is maximum and at ϵ_- it is minimum. It is important to note that these extremum properties are independent of the sign of k From the expression (6), the nature of $f(\epsilon)$ is now quite clear. Equations (9) and (10) show that $\epsilon_+ > 0$ and $\epsilon_- < 0$ when $k > 0$, otherwise when $k < 0$. So that when $k > 0$ as ϵ increases from $-\infty$, $f(\epsilon)$ decreases gradually from E_2 to a minimum at ϵ_-, then increases (passing through E_1 at $\epsilon = 0$) upto a maximum at ϵ_+, further, it gradually decreases to E_2 as $\epsilon \to +\infty$. Hence, the minimum is less than E_1. The nature of variation of $f(\epsilon)$ for $k < 0$ may be easily inferred from the fact that the expression (6) is invariant with simultaneous change of sign of k and ϵ. The expressions for f_{min} and f_{max} may be obtained easily as

$$f_{min} \equiv f(\epsilon_-) = E_1 - \tfrac{1}{2}\{\bar{E} - (E_2 - E_1)\}, \qquad \ldots(12)$$

and

$$f_{max} \equiv f(\epsilon_+) = E_2 + \tfrac{1}{2}\{\bar{E} + (E_2 - E_1)\}. \qquad \ldots(13)$$

From expression (10) $\bar{E} > (E_2 - E_1)$, hence

$$f_{min} < E_1 \quad \text{and} \quad f_{max} > E_2. \qquad \ldots(14, 15)$$

The corresponding variational states are

for

$$f_{min} : \quad \psi_- = (\phi_1 + \epsilon_-\phi_2)(1 + \epsilon_-^2)^{-\frac{1}{2}} \qquad \ldots(16)$$

for

$$f_{max} : \quad \psi_+ = (\phi_1 + \epsilon_+\phi_2)(1 + \epsilon_+^2)^{-\frac{1}{2}}. \qquad \ldots(17)$$

Further, they are again orthogonal, *i.e.*

$$(\psi_+ \cdot \psi_-) = 0. \qquad \ldots(18)$$

This follows from equations (9) and (10) in virtue of

$$\epsilon_+\epsilon_- = -1. \qquad \ldots(19)$$

Discussion

The expression (11) for f_{min} shows that the estimate of ground state energy is further lowered with the help of variational states ψ_-. Since the ground state energy is an absolute minimum this is a better estimation of the latter and from the expressions (10) and (12) this difference increases with k. It is of interest to note that the method can not be repeated further with the new variational state ψ_- and ψ_+, as

$$(\widetilde{\psi_+} \,.\, H\psi_-) + (\widetilde{\psi_-} \,.\, H\psi_+) = 0. \qquad \ldots(20)$$

This follows from the fact that

$$(\widetilde{\psi_+} \,.\, H\psi_-) = \frac{\bar{E}}{2k} \{(\widetilde{\phi_2} \,.\, H\widetilde{\phi_1}) - (\phi_1 H_2)\} \qquad \ldots(21)$$

is purely imaginary and

$$(\widetilde{\psi_-} \,.\, H\psi_+) = (\widetilde{\psi_+} \,.\, H\psi_-)^* \qquad \ldots(22)$$

It has already been indicated that the method is not useful when $k = 0$, as in this case the only solutions of equation (8) are $\epsilon = 0$ and $|\epsilon| \to \infty$, which lead to ϕ_1 and ϕ_2 for $\psi_\mp$.

As a matter of fact, in case of real variational states the method is equivalent to the diagonalization of H operator in the subspace of these two states. From this point of view the initial variational problem may be reformulated, such that in addition to equations (2) and (3),

$$(\widetilde{\phi_2} H\phi_1) = 0, \qquad \ldots(23)$$

i e. the variational states should diagonalize H in this two-dimensional subspace of real ϕ's. In general for complex ϕ's, it is shown in the appendix that working with ϵ as a complex number equation (23) is still valid. The choice of new variation states in equation (5) is nothing other than to satisfy equation (20) or (24) ; hence, it cannot be further iterated.

Finally, the usefulness of the method in improving the estimates of the ground state energy is quite clear when one more variational state, in addition to that for the estimation of the ground state energy, is known. However, once the variational state for a tolerable estimate of the ground state energy is known, one can suitably choose another variational state in the usual manner, which satisfies equation (3). If this new state does not satisfy equation (24), $(k \neq 0)$, *i. e.* H is not diagonalized in this two dimensional subspace, then the above method immediately yields an improved estimate of the ground state energy. It is evident from expression (12) that the magnitude of the extent of lowering of the ground state energy increase with k, *i. e.* the more the magnitude of the real part of the non-diagonal elements of H, in this subspace, in comparison to the difference of the diagonal elements, the better is the improvement for the estimation state energy.

Further, the method in principle may be extended to the case when more than two variational states are known initially. However, this will introduce complication in the computations. We refrain from doing that at this stage.

Appendix

As stated in section 2, let us consider the new variational state to be formed with a complex parameter. Thus, the new normalized variational state is

$$\psi = (\phi_1 + \epsilon\,\phi_2)\,(1 + \epsilon_0^2)^{-\frac{1}{2}} \qquad \ldots(A1)$$

$$\text{and} \quad (\tilde{\psi}.\,H\psi) = \{E_1 + \epsilon_0^2 E_2 + 2\epsilon_0 k_0 \cos(\theta + \eta)\}(1 + \epsilon_0^2)^{-1} \qquad \ldots(A2)$$

$$\text{where} \quad \epsilon = \epsilon_0 e^{i\theta} \text{ and } k_0 e^{i\eta} = (\tilde{\phi}_1 \cdot H\,\phi_2)$$

$$\text{and} \quad \epsilon\,(\tilde{\phi}_1 \,.\, H\,\phi_2) + \epsilon^*\,(\tilde{\phi}_2 \,.\, H\,\phi_1) = 2\epsilon_0\,k_0 \cos(\theta + \eta). \qquad \ldots(A3)$$

The extrema of the expression (A2) *qua* a function $f(\epsilon,\theta)$ of two variables are obtained from the conditions

$$\frac{\partial f(\epsilon,\theta)}{\partial \epsilon} = 0\,, \quad \frac{\partial f(\epsilon,\theta)}{\partial \theta} = 0 \qquad \ldots(A4)$$

The extremum positions are given by the roots of the simultaneous equations

$$\left.\begin{aligned} &\{\epsilon_0\,(E_2 - E_1) + (1 - \epsilon_0^2)\,k_0 \cos(\theta + \phi)\}(1 + \epsilon_0^{2-2} = 0 \\ \text{and} \quad &\epsilon_0\,k_0 \sin(\theta + \eta)/(1 + \epsilon_0^2) = 0 \end{aligned}\right\} \quad \ldots(A5)$$

The only solutions which are relevant to the problem are

$$\left.\begin{aligned} &\sin(\theta + \eta) = 0,\ i.\,e.,\ \cos(\theta + \eta) = \pm 1 \\ \text{and} \quad &(1 - \epsilon_\pm^2\,k_0 + \sigma\epsilon_\pm\,(E_2 - E_1) = 0 \end{aligned}\right\} \quad \ldots(A6)$$

with $\sigma = \pm 1$, the roots of which are

$$\epsilon_\pm = \{\sigma(E_2 - E_1) \pm \bar{E}_0\}/2k_0$$

$$\text{where} \quad \bar{E}_0 = |\,\{(E_2 - E_1)^2 + 4k_0^2\}^{1/2}\,|\,. \qquad \ldots(A8)$$

The other roots of equation (A5), namely (i) $\epsilon_0 = 0$ and $\cos(\theta_0 + \eta) = 0$ and (ii) $\epsilon_0 \rightarrow \infty$ leads asymptotically to values E_1 and E_2 respectively. for $f(\epsilon, \theta)$ as discussed in section 2.

In order that the extremum may be a minimum or a maximum, the quardratic form

$$\frac{\partial^2 f}{\partial \epsilon^2}(\triangle\epsilon)^2 + 2\,\frac{\partial f \partial f}{\partial \epsilon \partial \theta}\,\triangle\epsilon\,\triangle\theta + \frac{\partial^2 f}{\partial \theta^2}\,(\triangle\,\theta)^2$$

should be positive definite or negative definite at these points. Since

$$\left(\frac{\partial^2 f}{\partial \epsilon^2}\right)_{\theta_0, \epsilon_\pm} = -\frac{\sigma \bar{E}_0}{(1+\epsilon_\pm^2)^2}, \left(\frac{\partial^2 f}{\partial \epsilon \partial \theta}\right)_{\theta_0, \epsilon_\pm} = 0$$

and $$\left(\frac{\partial^2 f}{\partial \theta^2}\right)_{\theta_0, \epsilon_\pm} = -\frac{2\sigma \epsilon_\pm k_0}{1+\epsilon^2_\pm} \qquad \text{(A 9)}$$

It follows that f is minimum at $\sigma = -1$, ϵ_+ and f is maximum at $\sigma = +1$, ϵ_+. These values of f are given by

$$f_{min} = E_1 - \tfrac{1}{2}\{\bar{E}_0 - (E_2 - E_1)\} \qquad \text{...(A10)}$$

$$f_{max} = E_2 - \tfrac{1}{2}\{\bar{E}_0 + (E_2 - E_1)\}. \qquad \text{...(A11)}$$

Though they are exactly of the same form as given by equation (12) and (13), f_{min} in equation (A10) is in general less than f_{min} in equation (12). This is because in the expression (A8) for $\bar{E}_0$, $k_0 \geqslant k$ as $k = k_0 \cos \eta$, from equation (7) and (A3). In this case also the two variational states corresponding to these extrema are orthogonal,

$$(\tilde{\psi}_+ \cdot \psi_-) = 0 \qquad \text{.. (12)}$$

As before this is due to $\epsilon_+ \epsilon_- = -1$, which follows from the equation (A7). Thus the method of forming the new variational states is equivalent to the construction of states such that the Hamiltonian is diagonalized in this two dimensional subspace.